Improvement in the Ion Exchange Chromatographic Separation of Rare Earth Elements in Geological Materials for Their Determination by Inductively Coupled Plasma Atomic Emission Spectrometry*

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Ion exchange chromatographic separation of the rare earth elements (REEs) in geological materials for their determination by inductively coupled plasma atomic emission spectrometry has been improved. The time taken for the procedure, the consumption of reagents and the external contamination of the samples have been reduced. The emission of corrosive vapours has been totally eliminated. The efficiency of the chromatographic separation by elution with two concentrations of hydrochloric acid has been confirmed at higher flow rates in a high pressure chromatographic column. A prototype has been designed to combine the use of a pressure operated chromatographic column with the simultaneous evaporation of the eluates and the recovery of the acid. The column was charged with the solution resulting from the decomposition of the sample and the matrix elements were eluted with 2 mol l⁻¹ HCl and the REEs with 6 mol l⁻¹ HCl. The REE fraction from the column was concentrated by distillation. The whole process (separation and concentration) was performed in 1 h 15 min. The saving in time reached a factor of 30. The recoveries of the REEs during the ion-exchange procedure ranged from 96 to 105%. The accuracy and precision have been evaluated by analysing seven geological reference materials: NIM-G (Granite), NIM-L (Lujavrite), NIM-N (Norite), SY-2 (Syenite), SY-3 (Syenite), MRG-1 (Gabbro), and JB-1a (Basalt). Differences between obtained and certified values were not statistically significant for $\alpha = 0.05$ (t-test). The precision varied from 1.8 to 18.2%.

Keywords: *Inductively coupled plasma atomic emission spectrometry; rare earth elements; geological materials; cation exchange chromatographic separation; pressure elution*

The determination of rare earth elements (REEs) in geological samples is a very important contribution to the petrogenetic studies.¹⁻⁵ Inductively coupled plasma atomic emission spectrometry (ICP-AES) has been widely used for this determination.⁶⁻¹² However, the REE contents in the majority of geological materials are very low and there are many overlap-

ping and background spectral interferences from the matrix. Consequently, a direct determination of these elements by ICP-AES after simple decomposition of the sample is, in most cases, impossible.

The cation exchange chromatographic separation of the REEs, prior to their concentration by evaporation of the acid eluates, has been applied as sample pretreatment.⁶⁻¹⁴ This chromatographic separation has several disadvantages when its application to routine procedures is intended. One of them is the long time (several hours) required for the percolation of the gravity-operated columns. Most chromatographic columns are 10–20 cm in length and 1–2 cm in diameter, charged with a 100–200 or a 200–400 mesh cationic resin. These columns run at a flow of nearly 1 ml min⁻¹ and the required volume of eluate is > 500 ml, so, complete separation takes at least 8 h. Another disadvantage is the evaporation of the large volume of eluate, which takes an additional 8 h. Following this, the evaporated solution must be filtered to remove small particles of resin.¹ Some authors use a membrane or a sintered glass filter in the bottom of the column to avoid the mentioned filtration,⁷⁻¹⁰ but this will result in a slower flow. The most widely used solution to this problem is the use of a battery of columns in order to reduce the required time per sample. This involves a large working area and a lot of glassware. Perhaps the most important problem is the aggressive effect that several litres of concentrated hydrochloric or nitric acids being evaporated simultaneously have on the exhaust system and the environment of the laboratory.

The aim of this work is to improve the ion exchange chromatographic separation method for the ICP-AES determination of 14 REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) in geological materials by the development of a prototype that allows a reduction in procedure time, and the collection and recovery of acid vapours, thereby, preventing emission to the environment of the laboratory.

EXPERIMENTAL

Instrumentation

A schematic diagram of the instrumentation developed for the separation of REEs from the sample is shown in Fig. 1. This prototype basically consists of a glass column C, an evapor-

* Presented at the 1993 European Winter Conference on Plasma Spectrochemistry, Granada, Spain, January 10–15, 1993.

Fig. 1 Schematic diagram of the prototype: A, sample solution; B, peristaltic pump; C, borosilicate glass ion-exchange column; D, 2 mol l⁻¹ HCl; E, waste; F, 6 mol l⁻¹ HCl; G, evaporation and recovery system; N, REEs concentrate; and V1, V2, V3 and V4, valves

Fig. 2 Diagram of the evaporation and recovery system: H, distillator; I, condenser; and J, heater element

ation and recovery system G, a peristaltic pump B and four valves V1, V2, V3 and V4. A borosilicate glass ion-exchange column of 1 cm id by 21 cm in length is used. This column has a 70–100 μm sintered glass filter as bed support and a threaded tap with capillary tubing to introduce samples and acids. The evaporation and recovery system, G, (Fig. 2) is a home-made, high efficiency, continuous distillator which consists of a distillator H, a condenser I and a heater element J. The heater element, J, (Fig. 3) consists of a kanthal (Fe–Cr–Al alloy) type resistance L, wound onto an alumina ceramic tube M; this system is placed inside a quartz tube K. A Gilson Minipuls Model-3 peristaltic pump was employed. The way in which the designed prototype operates is described under Results and Discussion.

For the ICP-AES measurements, a Jobin-Yvon 70+ combination sequential-simultaneous spectrometer was employed. In order to minimize spectral interferences, only the JY 38 sequential system was used for all elements. The instrumentation and operating conditions are shown in Table 1.

Reagents

Standard stock solutions for each REE (1 mg ml⁻¹) were prepared from high-purity oxides (Johnson Matthey Chemicals, Specpure). High-purity HNO₃ (65%), HCl (37%),

Fig. 3 Diagram of the heater element: K, quartz tube; L, kanthal-type resistance; and M, alumina ceramic tube

Table 1 ICP-AES instrumentation and operating conditions

Plasma source	
Rf generator	Durr-JY 2300
Oscillator frequency/MHz	40.68
Incident power/W	1250
Reflected power/W	< 5
Monochromator	
Type	JY-38
Mounting	Czerny-Turner
Focal length/m	1
Grating	Holographic with 3600 grooves mm ⁻¹
Reciprocal linear dispersion/nm mm ⁻¹	0.26 (1st order)
Resolution/nm	0.0026
Spectral range/nm	175–500
Operating conditions	
Torch	Durr-JY/Plasmatherm, demountable, with alumina injector and sheathing gas tube
Sample introduction	Meinhard low salt concentric glass nebulizer, type TR 50 C1, with humidifier on the argon aerosol carrier inlet
Spray chamber	Scott type, coaxial
Sample delivery	Gilson Minipuls 3 peristaltic pump, 1.2 ml min ⁻¹
Plasma argon flow rate/l min ⁻¹	14
Sheathing argon flow rate/l min ⁻¹	0.5
Nebulizer argon flow rate/l min ⁻¹	0.35
Cooling water for coils/ml min ⁻¹	130
Observation height above load coil/mm	12
Integration time/ms	500

HF (48%), HClO₄ (60%), Na₂CO₃ and Na₂B₄O₇ (Merck, Analytical-reagent grade) were used for sample dissolution, elution and standard solutions. Solutions of Ca, Al, Fe (10 mg ml⁻¹), Ba and Sr (1 mg ml⁻¹), from Spex standard solutions, were employed as matrix components. Solutions of Ti and Zr (1 mg ml⁻¹) were also used for the study of spectral interferences. Dowex 50X8 200–400 cationic exchange resin,

purchased from Aldrich Chemical Co., was used as the bed in the chromatographic column. De-ionized water with a resistivity greater than 18 MΩ cm, produced by a pure water generator system Milli-Q Plus (Millipore), was used throughout for the solutions.

Samples

The following reference materials were used: NIM-G (Granite), NIM-L (Lujavrite) and NIM-N (Norite) from National Institute of Metallurgy, now Council for Mineral Technology (MINTEK), South Africa; SY-2, SY-3 (Syenites) and MRG-1 (Gabbro) from Canadian Certified Reference Material Project; and JB-1a (Basalt) from the Geological Survey of Japan.

Sample Dissolution

A method of silica volatilization with HF–HNO₃–HClO₄ was used. A sample mass of ≈1 g was accurately weighed into a platinum crucible and 3 ml of HClO₄, 2 ml of HNO₃ and 10 ml of HF were added. The crucible, covered with a platinum lid, was heated until the sample was totally dissolved and the solution was evaporated overnight on a sand bath almost to dryness. Then 3 ml of HClO₄ were added and the mixture was heated almost to dryness again. Finally, 1 ml of HCl and 10 ml of water were added to dissolve the salts. By this procedure, samples were completely dissolved or a very little residue remained. In all cases, samples were filtered, the filter ashed and the residue fused in the same platinum crucible with 0.6 g of Na₂B₄O₇ + Na₂CO₃ (2+1) mixture for 5 min at 1000 °C. The melt was disgregated with hot water, acidified with 2 mol l⁻¹ HCl and added to the filtrate. The solution was evaporated to a final volume of approximately 20–25 ml.

Procedure

In order to remove the matrix elements and to preconcentrate the REEs, the sample solution was subjected to a cation exchange chromatography with the prototype developed. The resulting solution containing the REEs was diluted to a 25 ml volume. Calibration graphs for the 14 REEs were established using a blank and a graded series of standards of appropriate concentration prepared from the REE standard stock solutions.

RESULTS AND DISCUSSION

Optimization of a Pressure Operated Chromatographic Column

In order to find the best conditions to operate the column under pressure, two experiments were carried out: operating at 0.5 ml min⁻¹ (0.1 kg cm⁻², near to gravity percolating flow); and operating at 8 ml min⁻¹ (1.5 kg cm⁻²). For chromatographic separation, a procedure based on the use of a gradual elution with HCl was adopted. It consisted of elution of the matrix with 2 mol l⁻¹ HCl and REE elution with 6 mol l⁻¹ HCl. The flow rate in this column, when operated by gravity, was very slow (0.22 ml min⁻¹). It was observed that the flow could be increased by applying moderate pressure.

To determine the efficiency of the column at higher flows, a simple device was adopted, in which the acid solutions were kept in bottles under pressure. The bottles had connecting tubings to the column and the acids were allowed to pass by means of taps. In this way it was possible to measure the flow and pressure. For a pressure of 0–3 kg cm⁻² a linear relation between flow and pressure was obtained with a value of 5.3 ml cm² kg⁻¹ min⁻¹.

Two sets of elution curves were obtained for the HCl separation. The column was loaded with a solution containing 1 mg of La, Nd, Ho, Lu, Sr and Ba, and 10 mg of Fe, Ca and Al, and then eluted by two different methods; with 200 ml of

Fig. 4 Elution curves of elements for a flow rate of (a) 0.5 ml min⁻¹ and (b) 8 ml min⁻¹

2 mol l⁻¹ HCl and with 400 ml of 6 mol l⁻¹ HCl solutions. Elution 1 was made at 0.5 ml min⁻¹ and elution 2 at 8 ml min⁻¹. The eluted solutions were collected in 20 ml fractions. The percentage amounts of eluted elements were plotted versus the eluted volume. The curves are shown in Fig. 4; for 0.5 ml min⁻¹ [Fig. 4(a)] and 8 ml min⁻¹ [Fig. 4(b)] the differences between the curves are negligible. That means that practically no efficiency in the separation is sacrificed when the flow is increased several times. This incremental increase in the flow, by applying moderate pressures to the column, allows a significant saving in the time required for the elution process.

Simultaneous Evaporation

To take advantage of a faster column, it is necessary to use an evaporating system that is as fast as the column and operates simultaneously. In this way, the time for elution is not added to the time for evaporation. The volume of the evaporating solution must be a small fraction of the total eluted volume. With these requirements a conventional, non-boiling evaporation is difficult.

In our prototype (Fig. 2), the eluate containing the REEs is continuously introduced into the bottom of the distillator H, where it is rapidly heated and evaporated by the heater element J. The temperature of evaporation is the azeotrope temperature of HCl and H₂O (108.584 °C). The vapour is condensed in the condenser I and the acid recovered in F, by forming a closed cycle. At the same time that the 6 mol l⁻¹ HCl is pumped, the eluate solution is being evaporated, and the volume of the boiling solution is always <15 ml. In our experience, the distillator ran without problems in the range 3–8 ml min⁻¹. The reason to employ HCl instead of HNO₃ or mixtures of both is because of its better behaviour during the distillation process.

Operation of the Prototype

The operation of the prototype is carried out in four consecutive steps. (1) The sample solution is pumped from A by the

peristaltic pump B and forced to pass through the column C. (2) The valve V1 is positioned to aspirate 2 mol l⁻¹ HCl from D. Valve V1 remains in this position until 160 ml of acid are pumped through the column C. In this operation, valve V3 is positioned to send the eluate solution containing matrix elements to waste E. (3) Valve V2 is positioned to aspirate 6 mol l⁻¹ HCl from F. At the same time, valves V3 and V4 are positioned to send the eluate solution containing the REEs to the evaporating system G, where it is introduced at the bottom of the distillator H. This solution is continuously heated and evaporated by the heater element J. The vapour is condensed in the condenser I and the acid recovered in F, by forming a closed cycle. A total of 400 ml of acid are pumped through the column C. However, the continuous evaporation in this closed system G keeps the volume of 6 mol l⁻¹ HCl used in this process at 50 ml. (4) At the end of the process, the small volume of acid solution containing the REEs concentrate, retained in the bottom of H, is removed by moving valve V4 and recovered in N.

When the separation and concentration process is finished, rinsing between samples is performed by running the system for several minutes with 6 mol l⁻¹ HCl and water.

Duration of the Procedure

When our 200–400 mesh resin column is operated at 8 ml min⁻¹, the complete process can be attained in <1 h 15 min. The time spent by a gravity operated column running at 0.5–1 ml min⁻¹ is 10 h approximately and, in addition, approximately 8 h are required to evaporate the acid. The time of the whole procedure (separation and evaporation) is increased fifteen times. It is necessary to point out that, in our experience, when the same column operating by gravity is equipped with a sintered glass filter, the process is much slower (0.22 ml min⁻¹ percolating flow); in this case, the saving in time, when our method is followed, can reach a factor of 30.

Analytical Lines

An experimental study on spectral interferences for the line giving the lowest detection limit¹⁵ for each REE was carried out. Fig. 4 shows that all the Fe, Al and Ca, and most of Sr and Ba, have been eluted before Lu, which is the first eluting REE. Only a small portion of Sr and Ba is present in the first eluates of REEs. Titanium and Zr are eluted mainly in the matrix fraction, and only a small part is eluted in the REE fraction. However, all these elements have been considered in this study. In this way, spectral scans in the vicinity of each wavelength with 1 µg ml⁻¹ single-element REE analyte solutions, 10 µg ml⁻¹ single-element solutions of Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ca, Sr, and Ba, 50 µg ml⁻¹ single-element solutions of La, Ce, Ti and Zr, and 100 µg ml⁻¹ single-element solutions of Al and Fe were performed until one line free from spectral interferences or, with easily corrigible interferences, was found.

The line of each REE giving the lowest detection limit¹⁵ exhibited partial or no spectral interferences and can be used as the analytical lines, excluding the following lines, which present total interferences and cannot be used for analytical determinations: the Pr II 390.844, 414.311 and 417.939 nm lines, which are interfered with by the Ce II 390.841 and 390.854, 414.283 and 417.929 nm lines, respectively; the Nd II 401.225 nm line, which is interfered with by the Ti II and Ce II 401.239 nm line; and the Er II 337.271 nm line, which is interfered with by the Ti II 337.280 nm line.

The lines that present partial spectral interferences can be easily corrected on the basis of the equation^{16,17}

$$c_i = a_i - \sum k_{ij}c_j$$

where *c_i* is the concentration of the analyte *i*, *a_i* the apparent concentration of the analyte *i*, *c_j* the concentration of interfering element *j*, and *k_{i,j}* the inter-element correction coefficient of the element *j* for the element *i*. The *k_{i,j}* values were determined

Table 2 Analytical lines, partial spectral interferences and inter-element correction coefficients *k_{i,j}*

Element	λ/nm	Partial interference	<i>k_{i,j}</i> /ng ml ⁻¹ of analyte element per µg ml ⁻¹ of interferent element
La II	333.749*	—	—
Ce II	413.765*	—	—
Pr II	422.535†	Sm II 422.533	547
Nd II	430.358†	Pr II 430.361	64.4
Sm II	359.260†	Nd II 359.259	47.6
		Gd II 359.271	67.6
Eu II	381.967*	—	—
Gd II	342.247†	Ce II 342.249	7.0
		Ce II 342.253	—
		Ce II 342.271	—
Tb II	350.917†	Sm II 350.910	27.0
		Ho ≈ 350.92†	44
Dy II	353.170†	Ce II 353.159	1.2
		Ce I 353.162	—
		Tb II 353.170	0.99
		Nd II 353.171	2
Ho II	345.600*	—	—
Er II	349.910†	Nd ≈ 349.91‡	3.1
Tm II	313.126†	Er II 313.107	6.5
		Tb II 313.135	5.4
Yb II	328.937*	—	—
Lu II	261.542*	—	—

* Line free from spectral interferences, suitable for analytical determinations.
† Line that might present partial spectral interferences, suitable for analytical determinations by applying the corresponding *k_{i,j}* value.
‡ Line not reported in the literature.

Table 3 Detection limits

Element	In solution/ng ml ⁻¹	In sample/µg g ⁻¹
La	2.5	0.06
Ce	9.6	0.24
Pr	16	0.4
Nd	6.7	0.17
Sm	2.6	0.06
Eu	0.3	0.007
Gd	5.1	0.13
Tb	1.9	0.05
Dy	0.4	0.01
Ho	1.8	0.04
Er	0.3	0.007
Tm	0.9	0.02
Yb	0.05	0.001
Lu	0.09	0.002

Table 4 REE recoveries using the ion-exchange procedure

Element	Added/µg ml ⁻¹	Found/µg ml ⁻¹	Recovery (%)
La	1.22	1.20	98
Ce	1.92	1.91	99
Pr	1.13	1.14	101
Nd	0.994	1.02	103
Sm	0.086	0.090	105
Eu	0.014	0.0134	96
Gd	0.0515	0.0523	101
Tb	0.067	0.065	97
Dy	0.082	0.079	96
Ho	0.0158	0.0161	102
Er	0.042	0.042	100
Tm	0.0079	0.0077	97
Yb	0.0816	0.0795	97
Lu	0.0082	0.0084	102

Table 5 REE concentrations ($\mu\text{g g}^{-1}$) in seven geological reference materials (analytical results expressed as mean $\pm$ standard deviation of five replicate determinations, and RSD values in parentheses) and comparison with other data

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
MRG-1														
This work	10.1 $\pm$ 0.6 (5.9)	27.2 $\pm$ 1.3 (4.8)	3.50 $\pm$ 0.12 (3.4)	18.7 $\pm$ 1.1 (5.9)	4.38 $\pm$ 0.23 (5.2)	1.34 $\pm$ 0.06 (4.5)	4.04 $\pm$ 0.14 (3.5)	0.47 $\pm$ 0.07 (14.9)	2.75 $\pm$ 0.11 (4.0)	0.49 $\pm$ 0.01 (2.0)	1.07 $\pm$ 0.09 (8.4)	0.12 $\pm$ 0.02 (16.7)	0.73 $\pm$ 0.10 (13.7)	0.11 $\pm$ 0.02 (18.2)
Ref. 18	9.8*	26	3.4	19.2*	4.5*	1.39*	4	0.51*	2.9	0.49*	1.12	0.11	0.6†	0.12
Ref. 19	9.8	26	3.4	19.2	4.5	1.39	4.0	0.51	2.76	0.49	1.12	0.11?	0.6?	0.13
Ref. 20	12.4	27.8	—	19.1	4.6	1.68	4.5	—	3.3	—	—	—	0.99	0.12
Ref. 12	8.8	24.8	3.73	19.3	4.63	1.43	4.19	—	2.97	0.50	1.22	—	0.83	0.12
NIM-G														
This work	107 $\pm$ 3 (2.8)	192 $\pm$ 6 (3.1)	18.7 $\pm$ 1.3 (6.9)	75.0 $\pm$ 4.8 (6.4)	15.3 $\pm$ 0.7 (4.6)	0.32 $\pm$ 0.04 (12.5)	14.7 $\pm$ 0.7 (4.8)	3.03 $\pm$ 0.16 (5.3)	18.0 $\pm$ 1.3 (7.2)	3.49 $\pm$ 0.21 (6.0)	11.2 $\pm$ 0.9 (8.0)	2.11 $\pm$ 0.15 (7.1)	14.4 $\pm$ 0.4 (2.8)	2.01 $\pm$ 0.06 (3.0)
Ref. 18	109*	195*	—	72*	15.8*	0.35*	14	3*	17	—	—	2*	14.2*	2
Ref. 19	109	195	19.5	72	15.8	0.35	14?	3.0	17?	3.60	10.5	2?	14.2	2?
Ref. 20	110	197	—	74.5	15.1	0.24	15.9	—	18.4	—	—	—	14.2	1.95
Ref. 12	110	200	21.7	73	15.2	0.31	15.0	—	19.2	4.25	13.4	—	14.2	2.07
SY-2														
This work	72.3 $\pm$ 4.1 (5.7)	170 $\pm$ 7 (4.1)	18.4 $\pm$ 0.9 (4.9)	74.8 $\pm$ 2.2 (2.9)	16.0 $\pm$ 0.4 (2.5)	2.53 $\pm$ 0.16 (6.3)	15.9 $\pm$ 1.1 (6.9)	2.47 $\pm$ 0.15 (6.1)	19.2 $\pm$ 1.6 (8.3)	4.10 $\pm$ 0.44 (10.7)	12.2 $\pm$ 0.9 (7.4)	2.14 $\pm$ 0.06 (2.8)	17.3 $\pm$ 0.6 (3.5)	2.58 $\pm$ 0.16 (6.2)
Ref. 18	75*	175	18.8*	73	16.1*	2.42	17*	2.5	18	3.8	12.4	2.1*	17†	2.7
Ref. 19	75	175	18.8	73	16.1	2.42	17	2.5?	18	3.8	12.4	2.1	17?	2.7
Ref. 20	71.6	161	—	79.5	17.1	2.70	17.8	—	21.3	—	—	—	19.9	3.2
Ref. 12	68.7	162	20.2	74.4	16.5	2.40	16.7	—	19.8	4.55	15.0	—	17.4	2.86
SY-3														
This work	1329 $\pm$ 36 (2.7)	2219 $\pm$ 41 (1.8)	228 $\pm$ 11 (4.8)	688 $\pm$ 22 (3.2)	110 $\pm$ 4 (3.6)	16.8 $\pm$ 0.8 (4.8)	109 $\pm$ 7 (6.4)	18.1 $\pm$ 0.6 (3.3)	121 $\pm$ 5 (4.1)	28.3 $\pm$ 1.9 (6.7)	78.2 $\pm$ 4.5 (5.7)	11.5 $\pm$ 0.5 (4.3)	64.7 $\pm$ 2.2 (3.4)	8.1 $\pm$ 0.6 (7.4)
Ref. 18	1340*	2230*	223*	670	109	17*	105*	18	118	29.5*	68	11.6*	62†	7.9
Ref. 19	1340	2230	223	670	109	17	105	18	118	29.5	76.8	11.6	62?	7.9?
Ref. 20	1386	2228	—	719	120	17.2	113	—	125	—	—	—	70.0	8.5
Ref. 12	1265	2190	220	720	125	16.2	115	—	130	27.2	85	—	65	8.0
JB-1a														
This work	36.1 $\pm$ 2.5 (6.9)	68.4 $\pm$ 2.1 (3.1)	7.1 $\pm$ 0.6 (8.4)	23.1 $\pm$ 1.3 (5.6)	4.83 $\pm$ 0.24 (5.0)	1.41 $\pm$ 0.09 (6.4)	4.36 $\pm$ 0.21 (4.8)	0.75 $\pm$ 0.07 (9.3)	4.22 $\pm$ 0.33 (7.8)	0.56 $\pm$ 0.09 (16.1)	2.02 $\pm$ 0.14 (6.9)	0.37 $\pm$ 0.05 (13.5)	2.05 $\pm$ 0.07 (3.4)	0.32 $\pm$ 0.02 (6.2)
Ref. 18	38	67	—	—	5.2	1.5	—	0.7	—	—	—	0.34	2	0.33
Ref. 19	38	67	—	24.0	5.2	1.5	4.48	0.70	4.4	—	2.10	0.34	2.0	0.33
Ref. 20	37.6	70.9	—	26.9	5.0	1.59	4.4	—	4.1	—	—	—	1.99	0.31
Ref. 21	33.3	60.1	6.21	22.7	4.35	1.28	4.04	0.62	—	0.69	1.94	0.28	1.81	0.37
NIM-L														
This work	242 $\pm$ 10 (4.1)	249 $\pm$ 6 (2.4)	17.4 $\pm$ 0.8 (4.6)	50.3 $\pm$ 4.6 (9.1)	4.7 $\pm$ 0.4 (8.5)	1.13 $\pm$ 0.13 (11.5)	3.18 $\pm$ 0.34 (10.7)	0.64 $\pm$ 0.07 (10.9)	3.01 $\pm$ 0.23 (7.6)	0.77 $\pm$ 0.13 (16.9)	2.45 $\pm$ 0.21 (8.6)	0.17 $\pm$ 0.03 (17.6)	2.86 $\pm$ 0.12 (4.2)	0.47 $\pm$ 0.06 (12.8)
Ref. 18	250	240	—	48*	5	1.2*	—	0.7	—	—	—	—	3	0.4
Ref. 19	250?	240?	16.4	48	5?	1.2	3.6	0.7?	3.1	0.9	2.6	—	3?	0.4?
Ref. 20	232	292	—	52	4.4	1.16	3.0	—	3.3	—	—	—	3.14	0.51
Ref. 12	215	270	19.0	45.5	3.8	0.95	2.35	—	2.75	0.55	1.55	—	2.60	0.70
NIM-N														
This work	3.01 $\pm$ 0.09 (3.0)	5.87 $\pm$ 0.39 (6.6)	0.69 $\pm$ 0.12 (17.4)	2.97 $\pm$ 0.21 (7.1)	0.84 $\pm$ 0.09 (10.7)	0.62 $\pm$ 0.05 (8.1)	0.97 $\pm$ 0.11 (11.3)	0.16 $\pm$ 0.02 (12.5)	0.98 $\pm$ 0.07 (7.1)	0.22 $\pm$ 0.03 (13.6)	0.63 $\pm$ 0.10 (15.9)	0.10 $\pm$ 0.01 (10.0)	0.79 $\pm$ 0.13 (16.4)	0.17 $\pm$ 0.03 (17.6)
Ref. 18	3	6	—	3	0.8*	0.63*	—	—	—	—	—	—	0.7	0.2
Ref. 19	3?	6?	0.77	0.3	0.8?	0.63	0.91	0.17	1.00	0.22	0.67	0.10	0.7?	0.2?
Ref. 20	3.9	4.8	—	3.1	0.88	0.65	1.0	—	1.2	—	—	—	0.80	0.11
Ref. 12	2.8	5.5	0.67	3.9	0.82	0.58	0.96	—	1.06	0.22	0.67	—	0.66	0.10

* recommended values.
† information values.

by measuring the emission intensities at the specified wavelength by using $1 \mu\text{g ml}^{-1}$ single-element solution of each REE analyte and $10 \mu\text{g ml}^{-1}$ single-element solution of each interferent.

Table 2 shows the analytical lines, the partial spectral interferences and the corresponding $k_{i,j}$ values.

Detection Limits

The detection limit was defined as the concentration which gave a net signal equal to three times the standard deviation of the background level ($3S_b$), and measured using 2 mol l^{-1} HCl solutions with a concentration of REEs of $1 \mu\text{g ml}^{-1}$. The experimental detection limits, in solution and in geological samples, are shown in Table 3. The detection limits in the samples are evaluated from the detection limits in solution *i.e.*, 1 g of geological sample is digested and diluted to 25 ml. The values are between 0.05 ng ml^{-1} for Yb and 16 ng ml^{-1} for Pr.

Analytical Results

In order to check the efficiency of the chromatography column in the separation of the REEs from the matrix, a recovery test was carried out. For this, a synthetic solution was prepared by mixing single-element solutions of the 14 REEs. The concentrations of the various REEs were in a range near to the average concentration of the elements in the seven reference materials. As the solutions of these geological samples also contain major element constituents (excepting silica), $10000 \mu\text{g ml}^{-1}$ of Ca, Al and Fe were added to the synthetic solution. Table 4 shows the starting concentrations and the analytical results after ion-exchange separation, together with the percentages of recovery ranging from 96 to 105%. This test shows the soundness of the column separation procedure using HCl as well as the two chosen concentrations (2 and 6 mol l^{-1}). Also, the same procedure was applied to one of the samples (SY-3, Syenite), and the results confirm the recovery data obtained with the synthetic solution.

The proposed method was applied to the determination of the 14 REEs in the seven reference materials. The accuracy and the overall precision of the method (including sample dissolution and chromatographic separation) were estimated by carrying out five replicate analyses of each reference material. The analytical results are recorded in Table 5, where they

are compared with the compilations by Govindaraju¹⁸ and Potts *et al.*¹⁹ and with results obtained by ICP-AES^{12,20} (and by high-performance liquid chromatography²¹ in the case of JB-1a Basalt). In this Table, uncertainty values correspond to one standard deviation obtained from the five replicate analyses, and relative standard deviation (RSD) values are expressed as percentages. As can be seen, the concentrations obtained agree well with the values cited in the literature. From obtained and certified values, a *t*-test was carried out. For $\alpha=0.05$, differences were not statistically significant. The precision varies from 1.8 to 18.2%.

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Paper 4/07695H

Received December 19, 1994

Accepted March 14, 1995